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(54) CATALYTIC LIQUID FOR SYNTHESIS OF CARBON NANOTUBE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a catalyst liquid used in the synthesis of carbon nanotubes by the thermal decomposition of a carbon-containing material, to obtain a catalytic substrate formed by using the catalytic liquid, to obtain a method for producing the catalytic substrate using the catalytic fluid and to obtain a method for synthesizing carbon nanotubes using the catalytic substrate.

SOLUTION: This catalytic liquid for the synthesis of carbon nanotubes comprises a micro-emulsion prepared by dispersing hyperfine catalyst particles for the synthesis of carbon nanotubes in a solvent. The catalytic substrate for the synthesis of carbon nanotubes has hyperfine catalyst particles formed from the catalytic liquid on the surface. A carbon-containing material is thermally decomposed in the presence of the catalytic substrate of form carbon nanotubes on the substrate.

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JAPANESE [JP,2001-062299,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] Catalytic liquid for carbon nanotube composition which consists of microemulsion which distributed the catalyst ultrafine particle for carbon nanotube composition in the solvent.

[Claim 2] The catalyst base material for carbon nanotube composition characterized by having the catalyst ultrafine particle formed from the catalytic liquid of claim 1 on a front face.
[Claim 3] The production approach of the catalyst base material characterized by making a catalyst ultrafine particle adhere on a base material using the catalytic liquid of claim 1.
[Claim 4] The synthetic approach of the carbon nanotube characterized by carrying out the pyrolysis of the carbon-containing ingredient under existence of the catalyst base material of claim 2, and making a carbon nanotube generate on this base material.

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3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
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[Field of the Invention] This invention relates to the synthetic approach of the carbon nanotube to which the pyrolysis of the carbon-containing ingredient is carried out under existencc of thc catalyst base material formed using the catalytic liquid and this catalytic liquid which are used in case the pyrolysis of the carbon-containing ingredient is carried out and a carbon nanotube is compounded, and this catalyst base material.
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[Description of the Prior Art] In order to compound a carbon nanotube, a carbon-containing ingredient is pyrolyzed under existence of the base material which has a catalyst particle for carbon nanotube composition on a front face, and the method [chemical vapor deposition (CVD method)] of growing up a carbon nanotube on the base material is learned. As the production approach of the base material in this case, detailed pore is made to the (i) base material, and the approach of forming a minute catalyst particle on a base material by etching of the approach of embedding a catalyst particle there and the (ii) metal plate etc. is learned. Although the carbon nanotube film got blocked perpendicularly on the base material and densely is obtained when using such a catalyst base material, there is a problem that production of the base material takes big difficulty.
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[Problem(s) to be Solved by the Invention] This invention makes it the technical problem to offer the production approach of the catalyst base material formed using the catalytic liquid and this catalytic liquid which are used in case the pyrolysis of the carbon-containing ingredient is carried out and a carbon nanotube is compounded, and the catalyst base material using this catalytic liquid, and the synthetic approach of the carbon nanotube using this catalyst base material.
[0004]
[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. That is, according to this invention, the catalytic liquid for carbon nanotube composition which consists of microemulsion which distributed the catalyst ultrafine particle for carbon nanotube composition in the solvent is offered. Moreover, according to this invention, the catalyst base material for carbon nanotube composition characterized by having the catalyst ultrafine particle formed from said catalytic liquid on a front face is offered. Furthermore, according to this invention, the production approach of the catalyst base material characterized by making a catalyst ultrafine particle adhere on a base material using said catalytic liquid is offered. According to this invention, the synthetic approach of the carbon nanotube characterized by carrying out the pyrolysis of the carbon-containing ingredient under existence of said catalyst base material, and making a carbon nanotube generate on this base material is offered further again.
[0005]
[Embodiment of the Invention] The catalytic liquid of this invention consists of microemulsion which distributed the catalyst ultrafine particle used as the catalyst at the time of pyrolyzing a carbon-containing ingredient and compounding a carbon nanotube in the solvent. In this catalytic liquid, transition metals are usually used as that catalyst. Especially as this catalyst metal, a VIII group's metal, for example, nickel, cobalt, molybdenum, Fe, Cu, V, Pd, etc. are mentioned from V. The catalyst used by this invention can be a metal, and also they can be a metaled compound, for example, a metal boride, a metallic oxide, etc., and as long as it has a catalysis in composition of a carbon nanotube, what kind of thing is sufficient as it. Distributing the catalyst by the shape of an ultrafine particle in a solvent, the mean particle diameter is usually about 1-20nm. The concentration in liquid of the catalyst ultrafine particle is 1 - 5 % of the weight preferably 0.1 to 10% of the weight. As the solvent, water and various kinds of organic solvents are used. Alcohol, a ketone, ester, a hydrocarbon, etc. are included by the organic solvent. As the example, a methanol, propyl alcohol, amyl alcohol, a hexanol, a cyclohexanol, heptanol, octyl alcohol, a cyclohexane, a methyl ethyl ketone, a diethyl ketone,

cycloheptane, n-hexane, n-heptane, an isooctane, n-Deccan, benzene, toluene, a xylene, etc. are mentioned, for example. Use of the organic solvent which is in the range the boiling point of whose is 50-200 degrees C in this invention is desirable.

[0006] The approach of arbitration can be used that what is necessary is just the approach which may distribute a catalyst ultrafine particle to homogeneity in a solvent as the preparation approach of the catalytic liquid of this invention. A surfactant is added to an organic solvent and it is made to dissolve in it first in the desirable preparation approach. Next, the catalyst metallic compounds of fusibility are added to that organic solvent, and it is made to dissolve in it to the organic solvent containing this surfactant. Subsequently, the catalyst metallic compounds in this organic solvent are returned, and the microemulsion containing a catalyst ultra-fine particle is obtained by making an insoluble ultrafine particle-like catalyst metal generate. as said surface active agent -- an ionic surfactant -- a cationic surface active agent and an anionic surface active agent are used preferably. In this case, as a cationic surfactant, carbon numbers 8-22 and the quarternary ammonium salt which has the long-chain alkyl group and alkenyl radical of 12-20 preferably can be used. As an example of a cationic surface active agent, a JIDESHIRU dimethylannmonium star's picture, JIDESHIRU dimethylannmonium chloride, a didodecyl dimethylannmonium star's picture (or chloride), a cetyl trimethylammonium star's picture (or chloride), a dodecyl trimethylammonium star's picture (or chloride), etc. can be mentioned. Dioctyl sulfo SASSHINETO sodium salt etc. is mentioned as an example of an anionic surface active agent. The operating rate of a surfactant is 7 - 15 % of the weight preferably one to 20% of the weight among a solution. As said fusibility catalyst metallic compounds, the halogenides (a chloride, bromide, etc.) of a catalyst metal, organic-acid salts (acetate etc.), organic complex salt, nitrates (acetyl acetate salt etc.), etc. are mentioned.

[0007] Although the approach using the chemical reducing agents using hydrogen gas as reduction of the catalyst metallic compounds in a solution, such as a hydrazine besides reduction and a sodium borohydride, is mentioned, use of a chemical reducing agent is desirable. The reduction approach using this chemical reducing agent is enforced in ordinary temperature more than 1 mol twice of the amount of theory, and by adding a twice as many chemical 2-10-mol reducing agent as this under stirring in a solution preferably. In this case, that chemical reducing agent can be added with the gestalt of a water solution or an organic solvent solution.

[0008] Although it can be used as catalytic liquid as it is, since the microemulsion containing the catalyst ultrafine particle which is the above, and is made and obtained contains in composition of a carbon nanotube, and production of the particle film the surfactant which is not desirable, as for this thing, it is desirable [microemulsion] to remove and use that surfactant. Removal of the surface active agent from microemulsion carries out centrifugal processing of the microemulsion, and after it separates into a catalyst phase and a solvent phase and it removes the solvent phase, into a solvent, it is made to distribute again and it makes the catalyst phase microemulsion. Surfactant concentration usually obtains 0.1 or less % of the weight of catalytic liquid for such actuation preferably 1 or less % of the weight multiple times and by repeating 3 to 5 times preferably 2 to 8 times. It is also possible to carry out extract concentration of the ultrafine particle with the dialysis using the ultra filter as the other approaches.

[0009] In the preparation approach of other desirable catalytic liquid by this invention, water-soluble catalyst metallic compounds are beforehand used as a water solution, this water solution is distributed by the shape of an ultrafine particle in an organic solvent under existence of a surface active agent, and it carries out by carrying out after treatment of the obtained microemulsion like the above. 0.05 mols /or less of concentration of the catalyst metallic compounds in a water solution are [1.] 0.02 mols/l. or less preferably, and although especially the lower limit is not restrained, it is usually about 0.0001 mols/l.

[0010] In the above, although how to return the catalyst metallic compounds which dissolve into liquid, and return to a metal condition was shown, it can replace with the reduction to the metal by this reduction, and the usual settling which makes precipitate of insoluble metallic compounds, such as a metal hydroxide, and a metallic oxide, metallic sulfide, generate can also be adopted.

[0011] In order to produce a catalyst base material using the catalytic liquid of this invention, catalytic liquid is applied on a base material and it dries. As a base material, various kinds of well-known things can be used conventionally. Although not restrained especially, what has a hydrophobic front face is [that what is necessary is just heat-resistant ingredients, such as silicone, and ceramics, stainless steel, as this base material] desirable. In this invention, what has such an ingredient on the front face at least is used. The configuration can be the shape of the shape of a sheet, and a board, a column, tubed, etc. In this invention, a plate-like large area base material can be used advantageously. This large area base material is advantageously used as a catalyst base material at the time of producing the electron source for field emission used for a flat-surface display. As an approach of applying catalytic liquid on a base material, various kinds of well-known approaches can be used conventionally. As such an approach, the brush applying method, a roll coating method, a spray coating cloth method, a spin coat method, the method of sinking in the base material which carried out surface treatment, etc. are included. In this invention, print processes, such as screen-stencil, the ink jet method make a liquid blow off from a minute nozzle, etc. are preferably employable. When applying catalytic liquid on

a base material, it can apply to homogeneity all over the to a base material, and also the catalytic liquid can be applied the shape of the shape of a line, band-like, and a grid, and a dot, and in the shape of [of other arbitration] a pattern. The base material with which catalytic liquid was applied can obtain the catalyst base material with which the catalyst ultrafine particle adhered to the front face by drying this. The catalyst particle on a base material can be in the condition of a metallic sulfide metallurgy group boride besides a metal condition, a metallic oxide, a metal hydroxide, etc. that what is necessary is just in the condition of promoting generation of a carbon nanotube. In the case of metallic sulfide, it can obtain by making sulfidizing agents, such as a hydrogen sulfide, react to the ultrafine particle of the metal condition on the base material. The coating weight of the catalyst ultrafine particle on a base material is 10-10 to ten - one mol per two in rate 100cm.

[0012] In order to manufacture a carbon nanotube using the catalyst base material of this invention, the pyrolysis of the carbon-containing ingredient is carried out by the shape of a gas under existence of the catalyst base material.

[0013] Especially the carbon-containing ingredient used by this invention is not restrained, but should just be carbonized at an elevated temperature. As such a thing, aromatic hydrocarbon, such as acetylene series compound; benzene [, such as unsaturated hydrocarbon; acetylene], such as saturated hydrocarbon; ethylene, such as methane besides a carbon monoxide, ethane, a propane, and butane, a propylene, a butene, and isobutene, toluene, a xylene, and naphthalene, such mixture (for example, naphtha, gas oil, etc.), etc. are included. In this invention, use of the organic carbon ingredient from points, such as an ease of handling, and a point of a price, carbon content, and the liquefied aromatic hydrocarbon whose boiling point is 80-144 degrees C, for example, BENZERU, toluene, xylenes, and those mixture is desirable especially.

[0014] As the approach of carrying out the pyrolysis of the carbon-containing ingredient, a well-known approach is used conventionally. The usual heating approach by an electric furnace etc., the heating approach by microwave, the laser-heating approach, etc. are included by such approach. In the usual heating approach, 600-1000 degrees C whenever [stoving temperature] is 700-900 degrees C preferably. When pyrolyzing said carbon-containing ingredient, hydrogen gas can be mixed as carrier gas into the gas of the carbon-containing ingredient. moreover -- a carbon-containing ingredient -- sulfur compounds, such as a hydrogen sulfide and a mercaptan, -- optimum dose ****** -- things are made. Thereby, a straight carbon nanotube can be obtained on a base material.

[0015]

[Example] Next, an example explains this invention to a detail further.

[0016] In preparation toluene 9g of example 1 (1) catalytic liquid, 1g (DDAB) of JIDESHIRU dimethylannmonium star's pictures which are a cationic surface active agent is melted, and they are stirred for 1 hour. Next, 12mg of cobalt chloride 6 hydrates is introduced into a solution, and they are stirred for further 1 hour. This solution shows a transparent light blue. Then, 15micro of sodium-borohydride water solutions of 10M is dropped 1 times, and a cobalt chloride is returned. After dropping, a solution is suspended black and produces the precipitate of silver white. Next, after covering the solution containing this precipitate over an at-long-intervals alignment separator by 12000rpm for 10 minutes and removing a supernatant, by repeating the process which adds toluene, re-distributes and carries out centrifugal processing 4 times, an excessive surface active agent is removed and a cobalt particle is refined. Thus, in the obtained catalytic liquid, the mean particle diameter of the cobalt particle is about 4nm. Moreover, the surfactant concentration is less than [zero %1wt%] on parenchyma.

[0017] (2) After dropping the catalytic liquid obtained with the production above (1) of a catalyst base material on the silicon base material of 5mm around and forming the uniform catalytic liquid film, this was dried at the room temperature and the cobalt particle was made to adhere to the base material side. Thereby, the catalyst base material with which the cobalt particle adhered to the front face at homogeneity was able to be obtained. Next, to the cobalt particle of this catalyst base material, circulation contact of a hydrogen sulfide / the hydrogen mixed gas (hydrogen-sulfide concentration: ten-mol %) was carried out at 400 degrees C for 2 hours, reduction of a hydrogen sulfide and sulfuration of a cobalt particle were performed to coincidence, and the catalyst base material with which the cobalt sulfide particle adhered to the front face was obtained.

[0018] (3) After putting into the coil the catalyst base material obtained with the synthetic above (2) of a carbon nanotube and carrying out a temperature up to 900 degrees C in a nitrogen air current, it reacted by circulating acetylene / N2 mixed gas (acetylene concentration: one-mol %) at 900 degrees C for 1 hour. In this case, that total circulation capacity is 3 150cm. By this reaction, the carbon nanotube generated on the base material. It was checked that this carbon nanotube is what is the straight tube which carried out orientation perpendicularly on a silicon base material, and makes a subject a tube with a diameter [of 20-50nm] and a die length of 0.5-5 micrometers with a scanning electron microscope (SEM).

[0019] In example 2 example 1, it experimented similarly except having used the non-sulfurated catalyst base material. Also in this case, it was checked that a carbon nanotube is generated on that base material.

[0020]

[Effect of the Invention] By using the catalytic liquid of this invention, the pattern of a catalyst ultrafine particle which becomes easy and is made to adhere on the base material can also make manufacture of a catalyst base material the configuration of arbitration. Furthermore, it is also easy to obtain a large area base material. A carbon nanotube can be made to generate in the shape of [of arbitration] a pattern on the base material by carrying out the pyrolysis of the carbon-containing ingredient under existence of the catalyst base material of this invention.

[Translation done.]